frequencies hardly change from one symmetry species to another. The M-N stretching and N-M-N bending frequencies do vary with symmetry species but the primary isotope effects are due to change in force constants of only the bonds involving isotopically substituted atom[4] and therefore these skeletal modes have little effect on the value of the separation factor.

The equilibrium isotope effect is a function of the vibrational frequencies of the isotopic molecules and the contribution by the factor $ui/u'i$ is dominant at ordinary temperatures[4,10]. This is evident from expressions (4) and (6). The ratio $ui/u'i$ also gives the harmonicity of the i^{th} vibration with the value 1·414 for perfectly harmonic vibration and decreases with increasing anharmonicity. In particular case of ammines the primary isotope effect would result from the NH vibrations only. Thus the anharmonicity of these vibrations, when ammonia is coordinated to different cations, should be an indication of the magnitude of the isotope effects in different ammines, though a quantitative agreement should not be expected due to obvious reasons. From Table 2 we see that the ratio νH/νD (hereafter referred to as harmonicity) is in the order $Ni^{2+} > Co^{3+} > Rh^{3+} > Mg^{2+} > Ir^{3+}$ for symmetric stretching vibrations, whereas the separation factors are in the order $Ni^{2+} > Co^{3+} > Rh^{3+} > Ir^{3+} > Mg^{2+}$. The failure of above reasoning in the case of the last two complexes is due to neglect of all other NH vibrations except the symmetric stretching ones. The harmonicity of Ir complex is greater than that of Mg in the case of asymmetric stretching, degenerate bending and rocking vibrations while it is less in the case of symmetric stretching and symmetric bending. Since all the vibrations affect equally the calculation of the equilibrium constant, the isotope effect may not be strictly assigned due to only one of the many vibrations. However, from Table 2 it can be seen that the NH_3 rocking vibration shows trends exactly identical to the isotope effect. This treatment is particularly complex in that there are five different vibrations involving appreciable movement of isotopically substituted atoms; with lesser number of vibrations in smaller molecules the relationship between isotope effect and harmonicity of the vibrations in a series of similar compounds is expected to be more straightforward.

The high value of the separation factors obtained indicate suitability of these exchange reactions as a method for enriching deuterium on a large scale. For Co^{3+}, Rh^{3+} and Ir^{3+} hexaammine complexes, the rate of exchange of ammonia molecules (or lability) is small[1], requiring use of a catalyst. However, in the Ni^{2+} complex, for which the separation factor is also largest, the ammonia ligands are highly labile by themselves[1], with the rate constant.

$$k = \frac{\text{Reaction rate}}{6[\text{Ni}]} = 1{\cdot}0 \times 10^5 \text{ sec}^{-1} \text{ at } 25^\circ \text{ (ref. 13)}$$

Table 2 — Harmonicity of Different Vibrations in Relation to Isotope Effect

νH/νD	Ni^{2+}	Co^{3+}	Rh^{3+}	Ir^{3+}	Mg^{2+}
NH sym. stretch	1·401	1·394	1·376	1·353	1·372
NH_3 rock	1·324	1·315	1·299	1·295	1·289

Therefore this reaction is much more suitable than the rest for the above purpose.

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Application of Henderson's Partition Function in the Computation of Sound Velocity & Solubility Parameter

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Sound velocity in liquid hydrogen and solubility parameters of liquid solvents such as CS_2, ether, C_6H_6, CH_3Cl, Br_2, N_2O, C_2H_6, dimethyl ether, CO, He, Cl_2, O_2, N_2, A and H_2 have been calculated using Henderson's partition function. Calculated values are in agreement with the observed values.

In our previous work[1-3], it was shown that the significant liquid structure theory as developed by Henderson[4] for rigid sphere molecules could reproduce the properties of real fluids in a good measure. It is, however, important for a theory of this type, which is based on an intuitive division of the partition function into gas-like and solid-like degrees of freedom, to be of general nature and valid for diverse kind of properties. With this end in view, we report our computation of sound velocity in liquids and solubility parameters of various liquid solvents.

Sound velocity — It has been established[5] that sound velocity (C_0) in a medium is given by the relation (1)

$$C_0 = \left[\frac{\gamma}{\beta_T \rho}\right]^{\frac{1}{2}} = \left[\frac{C_p}{C_v \beta_T \rho}\right]^{\frac{1}{2}} \qquad \ldots(1)$$

where γ is C_p/C_v, β_T is isothermal compressibility, ρ is density of liquid and C_p and C_v are heat capacities at constant pressure and volume respectively. Again, C_p is related with C_v by relation (2)

$$C_p = C_v + \frac{\alpha^2 VT}{\beta_T} = C_v + \frac{\alpha^2 MT}{\beta_T \rho} \qquad \ldots(2)$$

where α = coefficient of expansion, V = molar volume of liquid at a temperature T°K and M, molecular weight.

The values of C_p, α and β_T have been obtained from ref. 2 where they have been calculated using Henderson partition function[4]. C_p has been calculated using the known values of C_v and other quantities. The calculated and observed values of sound velocity in liquid hydrogen are given in Table 1.

Solubility parameter — The solubility parameter δ_T is related to heat of vaporization by Eq.[9] (3).

$$\delta_T = \left[\frac{\Delta E}{V_l}\right]^{\frac{1}{2}} = \left[\frac{\Delta H_v - RT}{V_l}\right]^{\frac{1}{2}} \quad ...(3)$$

where ΔH_v is the heat of vaporization and V_l = molar volume of the liquid at the temperature T°K. ΔH_v is given by Eq. (4)[1,2]

$$\Delta H_v = RT \ln \frac{V_g}{V_l} + \frac{3RTV_0}{2}\left(\ln 0{\cdot}00967\right)\left(\frac{1}{V_g} - \frac{1}{V_l}\right) + \frac{3RT}{2}\left[\frac{V_0}{V_g}\ln\left(8 - 11\frac{V_0}{V_g}\right) - \frac{V_0}{V_l}\ln\left(8 - 11\frac{V_0}{V_l}\right)\right] \quad ...(4)$$

where V_l is the molar volume of the liquid at temperature T(°K). Assuming that the vapour behaves ideally, the volume of vapour V_g is calculated from the vapour pressure of the liquid at a given temperature. The vapour pressure data[10], the molar volumes of liquids and observed solubility parameters[9] and the rigid sphere diameters[6] have been taken from standard reference works.

Utilizing Eqs. (3) and (4), the solubility parameter has been calculated for various solvents and are given in Table 2 along with the observed parameters.

The results in Table 1 show fair agreement between the calculated and observed values of sound velocity in liquid hydrogen while in other liquids, the results are erratic. For example, the calculated values of sound velocity in liquid argon, nitrogen, oxygen and methane are too high.

The calculated solubility parameters are generally in good agreement with those tabulated by Hildebrand and Scott[9] as shown in Table 2. The decreasing order of solubility parameter for various liquids used in this study and quoted in Hildebrand and Scott[9] is found to hold good with the exception of CS_2, CH_3Cl and C_2H_6.

Observed order (δ_T): $Br_2 > CS_2 = N_2O > Cl_2 > C_6H_6 > (CH_3)_2O > CH_3Cl > C_2H_6 > (C_2H_5)_2O > O_2 > A > CO > N_2 > H_2 > He$

Calculated order (δ_T): $Br_2 > N_2O > Cl_2 > CS_2 > C_6H_6 > (CH_3)_2O > (C_2H_5)_2O > O_2 > A > CH_3Cl > C_2H_6 > CO > N_2 > H_2 > He$

It can thus be concluded that a reliable estimate of δ_T is also possible through computation of ΔH_v based on the hole model of the liquid state.

Table 1 — Sound Velocity in Liquid Normal Hydrogen

Temp. °K	Density[a] g/cm³	Expansivity[c] $\alpha \times 10^3$ (°K)$^{-1}$	Compressibility[c] $\beta_T \times 10^4$ (atm^{-1})	Heat capacity (cal/mole)		Sound velocity (m/sec)	
				C_p	C_v	Present work	Observed[b]
14	0·07719	10·6	9·3	4·05	2·981	1385	1265
15	0·07634	11·5	10·3	4·20	2·969	1350	1246
16	0·07545	12·4	11·4	4·36	2·965	1316	1226
17	0·07450	13·2	12·5	4·52	2·968	1286	1204
18	0·07351	14·0	13·7	4·68	2·971	1258	1182
19	0·07248	14·9	15·0	4·86	2·967	1235	1158
20	0·07141	15·7	16·6	5·03	3·001	1197	1132

a, ref. 7; b, ref. 8; and c, ref. 2.

Table 2 — Solubility Parameters of Various Liquids

Liquid	Diameter[b] (Å)	Volume of liquid[a] cc/mole	Temp. °K	Vapour pressure[c]	Solubility parameter	
					Calc.	Obs.[a]
CS_2	4·437	61	298	364·2 mm	9·7	10·0
$(C_2H_5)_2O$	5·539	89	298	526·9 mm	7·7	7·4
C_6H_6	5·270	89	298	96·09 mm	9·2	9·15
CH_3Cl	3·375	56	298	(5·55 atm)	7·1	8·6
Br_2	4·268	51	298	(210 mm)	11·4	11·5
N_2O	3·816	36	184	(1·05 atm)	10·0	10·0
C_2H_6	3·954	55	184	(1 atm)	6·9	7·6
$(CH_3)_2O$	4·264	60	248	(720 mm)	8·2	8·8
CO	3·59	34	82	(1·05 atm)	6·1	6·1
He	2·556	32	4·2	(650 mm)	0·8	0·5
Cl_2	4·115	46	239	(755 mm)	9·9	9·8
O_2	3·433	28	90	(765 mm)	7·4	7·2
N_2	3·681	35	77	(745 mm)	5·9	5·9
A	3·400	28	87	(730 mm)	7·2	7·0
H_2	2·87	28	20·4	(740 mm)	2·6	2·5

a, ref. 9; b, ref. 6; and c, ref. 10.
The values in parentheses are obtained by graphical interpolation.

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Chronopotentiometry with Programmed Current: Theoretical Study of an Electrode Process Complicated by a Catalytic Reaction

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Theoretical chronopotentiometric equation for an electrode process complicated by a catalytic process is given for ramp current (current varying linearly with time) and ac chronopotentiometry.

PROGRAMMED current chronopotentiometry[1-4] provides useful information on the chronopotentiometric behaviour of various kinetic schemes. In the present note theoretical equations for electrode processes complicated by catalytic reaction are solved for the following current impulses: (a) the current varying linearly with time (ramp current); and (b) alternating current of small amplitude is superimposed over a constant electrolysis current (ac chronopotentiometry).

Theoretical analysis — For the kinetic scheme

$$O + ne \rightarrow R$$
$$R + Z \rightleftharpoons O$$

in which Z reacts with R, but is itself not involved in the electrode process, Fick's[5] second law equations are

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} + k_f C_Z(x,t) C_R(x,t) - k_b C_O(x,t)$$

$$\frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2} - k_f C_Z(x,t) C_R(x,t) + k_b C_O(x,t)$$

If the bulk concentration of the species Z (C_Z^0) is much larger than that of the electroactive species O, C_Z (x, t) can then be replaced by C_Z^0 in Fick's equations. For a simple case the rate of backward chemical reaction is negligible, $D_O = D_R = D$, and R is not present initially, the above equations reduced to

$$\frac{\partial C_O(x,t)}{\partial t} = D \frac{\partial^2 C_O(x,t)}{\partial x^2} + k_f C_Z^0 C_R(x,t) \quad \ldots(1)$$

$$\frac{\partial C_R(x,t)}{\partial t} = D \frac{\partial^2 C_R(x,t)}{\partial x^2} - k_f C_Z^0 C_R(x,t) \quad \ldots(2)$$

The initial conditions are

$$\left.\begin{aligned} C_O(x,0) &= C^0 \\ C_R(x,0) &= 0 \end{aligned}\right\} \quad \ldots(3)$$

$$\left.\begin{aligned} C_R(x,t) &= 0 \\ C_O(x,t) &= C^0 \end{aligned}\right\} x \rightarrow \infty \quad \ldots(4)$$

Also the boundary condition is obtained by equating the sum of fluxes of O and R at the electrode surface to zero

$$D\left\{\frac{\partial C_O(x,t)}{\partial x}\right\}_{x=0} + D\left\{\frac{\partial C_R(x,t)}{\partial x}\right\}_{x=0} = 0 \quad \ldots(5)$$

(a) *Ramp current* ($i = \theta t$) — When the electrolysis current is varying linearly with time (ramp current), the flux of the reducible species O is given as

$$\left\{\frac{\partial C_O(x,t)}{\partial x}\right\}_{x=0} = \frac{\theta t}{nFAD} \quad \ldots(6)$$

For solving Eqs. (1) and (2) under the initial and boundary conditions (3)-(6), the following transformation is made

$$\Psi(x,t) = C_O(x,t) + C_R(x,t) \quad \ldots(7)$$

Solving the Laplace transform of diffusion Eqs. (1) and (2), under condition (7), one obtains

$$\bar{\Psi}(x,S) = C^0/S + M \exp\left[-x\frac{S^{\frac{1}{2}}}{D^{\frac{1}{2}}}\right] \quad \ldots(8)$$

and

$$\bar{C}_R(x,S) = N \exp\left[-x\frac{(S+k_f C_Z^0)^{\frac{1}{2}}}{D^{\frac{1}{2}}}\right] \quad \ldots(9)$$

where M and N are integration constants whose values are to be determined from the initial and boundary conditions (see Appendix). Thus

$$\bar{\Psi}(x,S) = C_O^0/S \quad \ldots(10)$$

$$\bar{C}_R(x,S) = \frac{\theta}{nFAD^{\frac{1}{2}}S^2(S+k_f C_Z^0)^{\frac{1}{2}}} \exp\left[-x\frac{(S+k_f C_Z^0)^{\frac{1}{2}}}{D^{\frac{1}{2}}}\right] \quad \ldots(11)$$

At $x = 0$, Eqs. (10) and (11) reduce to

$$\bar{\Psi}(0,S) = C_O^0/S \quad \ldots(12)$$

$$\bar{C}_R(0,S) = \frac{\theta}{nFAD^{\frac{1}{2}}S^2(S+k_f C_Z^0)^{\frac{1}{2}}} \quad \ldots(13)$$

Inverse transforms of Eqs. (12) and (13) are

$$\Psi(0,t) = C_O^0 \quad \ldots(14)$$

and

$$C_R(0,t) = \frac{\theta}{\pi^{\frac{1}{2}}nFAD^{\frac{1}{2}}}\left[\frac{\pi^{\frac{1}{2}}(2k_f C_Z^0 t - 1)}{(k_f C_Z^0)^{3/2}}\,\mathrm{erf}(k_f C_Z^0 t)^{\frac{1}{2}} + \frac{t^{\frac{1}{2}}\exp(-k_f C_Z^0 t)}{(k_f C_Z^0)}\right] \quad \ldots(15)$$